respectively, and the two bending modes, ν_2 and ν_4. We suggest that the lines at 365 and 311 cm^{-1} correspond to ν_3 and ν_1, respectively, of the Fe–S_4 tetrahedron. The intensity pattern is identical with that found for $FeCl_4^-$,[21,22,25] where the analogous modes appear at 385 and 330 cm^{-1}. Additionally, the infrared-active metal–sulfur stretching vibrations have been assigned to lines at 340 cm^{-1} for the tris(ethylxanthato)cobalt(III) and tris(ethylxanthato)chromium(III) complexes.[26] In cysteine, aminoethanethiol, and mercaptopropionic acid complexes of Hg(II), strong Raman-active bands which appear at *ca.* 330 cm^{-1} are assigned to Hg(II)–S stretching modes,[27] and the assignment of bands in this frequency region to iron–sulfur stretches is not unreasonable.

A search has not revealed vibrational measurements on model compounds in which Fe(III) is tetrahedrally surrounded by sulfurs. Unfortunately, ferric ion catalyzes the oxidation of cysteine to cystine,[28] so this system may not be readily studied. A preliminary laser-Raman spectrum of potassium thioferrite, $KFeS_2$, which contains polymeric Fe–S_4 tetrahedra[29] and has been suggested as a possible ferredoxin model,[30] contains bands at 360 and 303 cm^{-1} which possibly bear analogy to the rubredoxin modes, but other lines at both higher and lower frequencies also appear in this spectrum. The bending modes could not be resolved because of the strong elastic scattering at relatively low frequencies. For $FeCl_4^-$, ν_2 and ν_4 are found at 106 and 133 cm^{-1}, respectively,[21,23] and slightly lower values for these lines might be expected for the Fe–S_4 polyhedron.

Similar studies of a variety of these materials are in progress with the goal of identifying systematic structural analogies and differences, particularly including those systems for which single-crystal X-ray data are available. To the extent that metal–ligand frequencies may be transferred between simple model compounds and these more complex systems, frequency comparisons may permit structural predictions in lieu of diffraction results.

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Steric Hindrance and Solvation Effects with Hydrogen-Bonded Adducts

Sir:

In an earlier report,[1] the enthalpy of hydrogen-bond formation between 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP) and γ-collidine (2,4,6-trimethylpyridine) was reported to be the same in both CCl_4 and hexane. Since CCl_4 is known to interact with pyridine and pyridine derivatives,[2] it was suggested that this observation stems from steric interaction between CCl_4 and the 2,6-methyl groups of γ-collidine.[3] In addition, the same enthalpies of reaction were reported for HFIP–pyridine and HFIP–collidine, which suggested a steric interaction between HFIP and collidine.[3]

More recently, Arnett, *et al.*,[4] have suggested that the pyridine–CCl_4 interaction is small since the same enthalpies were obtained for the phenol–pyridine reaction using CCl_4 as solvent (I) and pure base as solvent (II). In order to understand these solvation effects as well as to determine the strength of the pyridine–CCl_4 interaction, we have redetermined the HFIP solution reaction enthalpies and have included in our study the acid 2,2,2-trifluoroethanol (TFE) with the bases pyridine and γ-collidine.

Concentration studies of the heats of solution, ΔH_{sol}, of pyridine and γ-collidine in CCl_4 and hexane as a function of concentration demonstrate that pyridine has a greater tendency to self-associate in either solvent.[5,6] The concentration studies also indicate that both bases self-associate less in CCl_4 than in hexane. The greater self-association of neat pyridine than neat collidine is also shown by the $\Delta H_{\text{sol},\infty}$ values found in Table I. This association could be between the nitrogen lone pair of one molecule and a hydrogen or the ring π^* system of another molecule.[7]

Table I. The Heats of Solution at Infinite Dilution of Pyridine and γ-Collidine in CCl_4 and Hexane

Solvent	Base	$\Delta H_{\text{sol},\infty}$, kcal mol^{-1}
CCl_4	Pyridine	$+0.25\ (\pm 0.002)$
Hexane	Pyridine	$+1.96\ (\pm 0.012)$
CCl_4	γ-Collidine	$-0.34\ (\pm 0.003)$
Hexane	γ-Collidine	$+0.93\ (\pm 0.012)$

The data of Table I indicate the occurrence of steric repulsion in the CCl_4–collidine solvation. The observed $\Delta H_{\text{sol},\infty}$ of pyridine and γ-collidine in CCl_4 is the resultant of an endothermic term due to dissociation of base molecules and an exothermic term due to CCl_4–base interactions. In hexane, the observed $\Delta H_{\text{sol},\infty}$'s should be due mainly to the endo-

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(3) Such a conclusion is based on an assumption of the cancellation of various heats of transfer [acid and adducts (hexane → CCl_4) or donors and adducts (gas → hexane)].

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(6) py (0.015–0.475 *M*) in CCl_4, $\Delta H = -0.233M + 0.25$; py (0.040–0.433 *M*) in C_6H_{14}, $\Delta H = -1.053M + 1.96$; coll (0.030–0.245 *M*) in CCl_4, $\Delta H = -0.009M - 0.34$; coll (0.030–0.365 *M*) in C_6H_{14}, $\Delta H = -0.545M + 0.93$.

(7) L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Amer. Chem. Soc.*, **82**, 3828 (1960).

thermic dissociation of base molecules. For both donors, the hexane $\Delta H_{\mathrm{sol},\infty}$ is more endothermic than the CCl_4 $\Delta H_{\mathrm{sol},\infty}$. Therefore, the heat of transfer from hexane to CCl_4 should reflect the strength of the CCl_4–base interactions. These heats are -1.71 kcal/mol for pyridine and -1.27 kcal/mol for γ-collidine. The smaller γ-collidine transfer enthalpy probably represents steric interaction (>0.44 kcal/mol) between a CCl_4 molecule and the 2,6-methyl groups of γ-collidine.

Relative adduct solvation energies can be obtained from Haber cycles using the data in the tables. The data in Table II show that for every reaction the enthalpy is larger in hexane than in CCl_4.[8] The difference in hydrogen-bond enthalpies in these two solvents ($\Delta H_{\mathrm{hex}} - \Delta H_{\mathrm{CCl_4}}$) increases in the following order: TFE–pyridine (-1.15 ± 0.06) < TFE–collidine (-1.28 ± 0.03) < HFIP–pyridine (-1.35 ± 0.04) < HFIP–collidine (-1.45 ± 0.06). From the data in Tables I and II and from[1,5] $\Delta H^{\mathrm{TFE}}(\mathrm{hex} \rightarrow CCl_4) = -0.92$ kcal mol^{-1} and $\Delta H^{\mathrm{HFIP}}(\mathrm{hex} \rightarrow CCl_4) = -0.39$ kcal mol^{-1}, it can be shown easily that this increasing difference results mainly from greater solvation by CCl_4 of the TFE adducts then the corresponding HFIP adducts and greater solvation by CCl_4 of the pyridine adducts than the γ-collidine adducts. The adduct transfer solvation energies (kcal mol^{-1}, hexane → CCl_4) are HF·coll = -0.21, HF·py = -0.75, TF·coll = -0.91, TF·py = -1.48. The order of these values is exactly reversed from what one would expect from adduct polarities and is interpreted in terms of solvations which depend on the "congestion" at or the shielding of the polar O–H–B groupings. HFIP is the more sterically hindered acid,[9] while γ-collidine is the more sterically hindered donor. The relative order of HF·py and TF·coll leads us to conclude that collidine affords more shielding of O–H–B than HFIP.

Table II. Hydrogen-Bond Enthalpies for the Acids TFE and HFIP and the Bases Pyridine and γ-Collidine in the Two Solvents CCl_4 and Hexane

Acid	Base	Solvent	$-\Delta H_f$,[b] kcal/mol
TFE	Pyridine	CCl_4	6.67 ± 0.02
TFE	Pyridine	Hexane	7.82 ± 0.04
HFIP	Pyridine	CCl_4	8.40[a] $\pm$ 0.02
HFIP	Pyridine	Hexane	9.75[a] $\pm$ 0.02
TFE	γ-Collidine	CCl_4	7.52 ± 0.01
TFE	γ-Collidine	Hexane	8.80 ± 0.02
HFIP	γ-Collidine	CCl_4	9.67 ± 0.03
HFIP	γ-Collidine	Hexane	11.12 ± 0.03

[a] Reference 1. [b] The limits on ΔH are precision estimates as determined from sharpness of fit; see ref 5.

Arnett, *et al.*,[4] have recently indicated that pyridine–CCl_4 interactions are small since the same enthalpy of hydrogen-bond formation for the phenol–pyridine reaction is found when CCl_4 is solvent as when pure base is solvent. When adding an acid to pure pyridine, the associated pyridine molecules must be dissociated before a hydrogen bond can form. The energy (~2 kcal) necessary to dissociate these molecules is comparable to the energy (~1.7 kcal) required to disrupt the pyridine–CCl_4 interactions. Thus, it is not surprising that the same enthalpy is obtained by both methods, and the equality demonstrates the importance of CCl_4–pyridine interactions. Whenever base–solvent interactions are suspected, the best approach seems to be method I, using various inert solvents for comparison.

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(8) The possibility that the hexane heats are larger than the CCl_4 heats because of adduct solvation by excess base aggregates in hexane was checked. That this complication is not present is demonstrated by excellent fits of the data to plots of A_0B_0V/Q *vs.* B_0: *cf.* K. F. Purcell, *et al.*, *J. Amer. Chem. Soc.*, **91**, 4019 (1969).

(9) The acid-transfer heats suggest greater solvation of TFE than HFIP, which is in keeping with greater hindrance for the latter.

1,3,5,7-Tetramethylbicyclo[5.1.0]octa-2,5-diene (Tetramethylhomotropilidene) by a 1,4-Homoelimination Reaction. The Stereochemical Analysis of a Cope Rearrangement[1]

Sir:

Degenerate Cope rearrangements, which may easily be studied using established nmr techniques, have become of general interest recently because of the possible bishomobenzene-like transition state or intermediate involved in the rearrangement.[2] In an attempted preparation of a potential bishomobenzene derivative we devised a novel cyclopropane ring opening reaction, a 1,4 homoelimination, as exemplified by the synthesis of 1,3,5,7-tetramethylbicyclo[5.1.0]octa-2,5-diene (tetramethylhomotropilidene). We now wish to report the preparation and nmr behavior of this compound.

Treatment of diol I[3] with dry hydrogen chloride in benzene solution at 0° gave dichloride II,[4] mp 93.5–94°, in 85% yield: nmr (CCl_4) τ 5.60 (2 H, s), 8.72 (12 H, s), 8.84 (2 H, d, $J = 6$ Hz), 9.78 (2 H, d, $J = 6$ Hz). The configuration of II was assigned as follows. The reaction of dichloride II with sodium borohydride in 70% aqueous diglyme[5] at room temperature gave hydrocarbon III[4] in 64% yield: nmr (CCl_4) τ 8.20 (2 H, d, $J = 14.5$ Hz), 8.88 (2 H, d, $J = 14.5$ Hz), 8.91 (12 H, s), 9.79 (2 H, d, $J = 4.5$ Hz), 10.01 (2 H, d, $J = 4.5$ Hz). The presence of an AB quartet for the methylene protons adjacent to the cyclopropane rings in III demonstrates the cis orientation of the latter. Upon irradiation of the methyl signal (τ 8.72) of II, an 11 ± 4% increase in the integral intensity of the methine signal (τ 5.60) was observed. This detection of a nuclear Overhauser effect[6] combined with the observation of a single methine absorption and the cis cyclopropane

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